Thermal Rearrangements of *N*-Aryl-1-alkynesulphenamides into Indoline-2-thiones

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Reaction of bromomagnesium benzenamides with 1-alkynyl thiocyanates affords the title sulphenamides. On heating in benzene, these sulphenamides undergo [3.3]-sigmatropic rearrangements followed by cyclisation of the intermediate thioketenes yielding indoline-2-thiones.

The Claisen rearrangement in its various forms is one of the most important C–C bond-forming reactions in organic synthesis by virtue of its simplicity and selectivity[1,2,3]. Although [3.3]-sigmatropic rearrangements of systems in which an acetylenic bond is incorporated are well known[4], analogous reactions of related systems containing two contiguous heteroatoms have not been investigated to our knowledge[5]. The title sulphenamides **3** would be of interest as they might undergo an 1-aza-1′-thia-[3.3]-sigmatropic rearrangement to give *o*-aminophenyl-substituted thioketenes **(4)** which could further cyclise to form indoline-2-thiones **(5)**. This anticipation was based on the facts that the smooth rearrangements of 1-allylthio-1-alkynes[6] and the thermal instability of the S–N bond in sulphenamides[7] are well known.

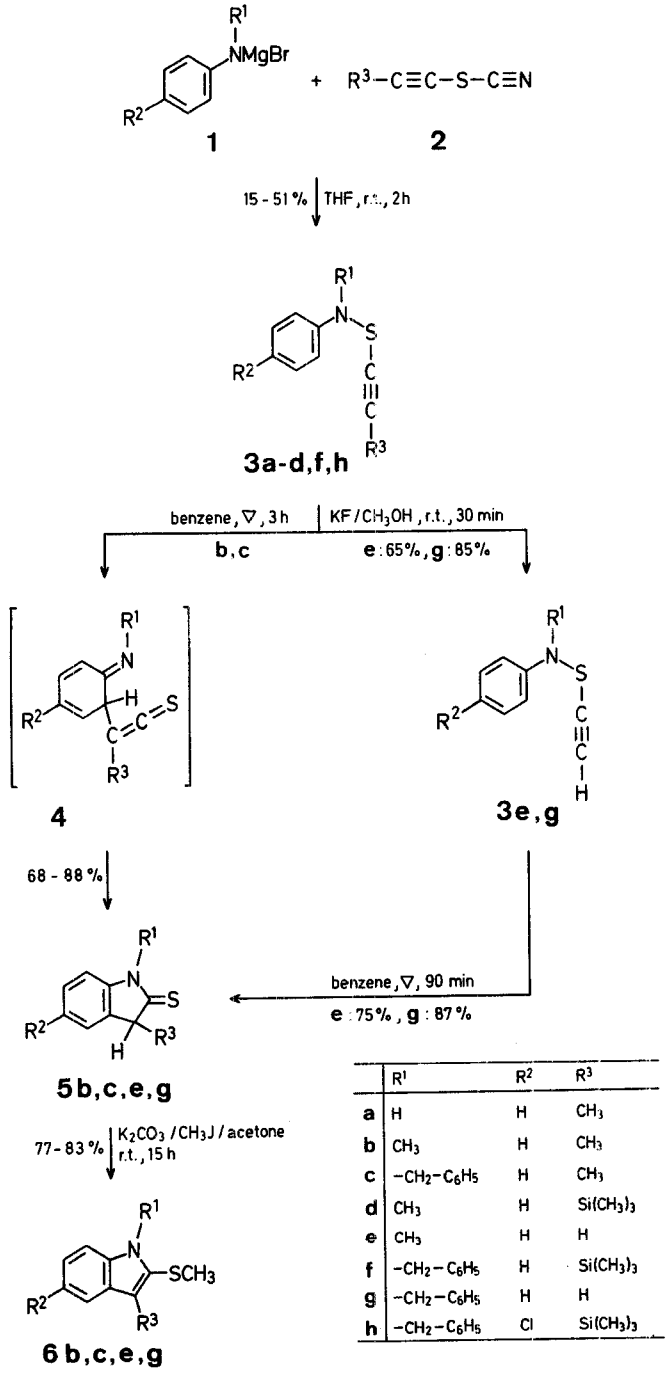
One of us has reported that the reaction of lithium dialkylamides with 1-alkynyl thiocyanates **(2)**[8,9,10] affords the corresponding sulphenamides[8,9]. It has now been found that the Grignard derivatives of *N*-substituted benzenamines **1** give better yields of *N*-aryl-1-alkynesulphenamides **(3)** than the *N*-lithiobenzenamines.

Preliminary experiments with the sulphenamide **3b** dissolved in various solvents (chloroform, carbon tetrachloride, benzene, toluene) showed that heating of a 0.1 molar solution in benzene for 3 h resulted in smooth transformation into the substituted indoline-2-thione **5b**. The structures of compound **5b** and of its methylated derivative **6** were ascertained by comparison of their spectral data with those of authentic compounds[11,12]. Similarly, compound **5c** was produced from **3c** in good yield.

The trimethylsilylacetylenesulphenamide **3f** was found to be stable after prolonged heating of its solution in benzene. Heating in toluene lead to decomposition. This result is of interest when compared with the reported smooth rearrangement of substituted allyl trimethylsilylethynyl sulphides to thioketenes[13].

Deprotection of the trimethylsilylacetylenesulphenamides **3d, f** with potassium fluoride in methanol affords the free acetylene sulphenamides **3e, g** which in boiling benzene are converted into the indoline-2-thiones **5e, g** more rapidly than the 1-propynesulphenamides **3b, c**.

The indolines-2-thiones are an interesting class of compounds whose chemistry has been reviewed[14] and which have found some applications in synthesis[15,16,17].



	R^1	R^2	R^3
a	H	H	CH_3
b	CH_3	H	CH_3
c	$-CH_2-C_6H_5$	H	CH_3
d	CH_3	H	$Si(CH_3)_3$
e	CH_3	H	H
f	$-CH_2-C_6H_5$	H	$Si(CH_3)_3$
g	$-CH_2-C_6H_5$	H	H
h	$-CH_2-C_6H_5$	Cl	$Si(CH_3)_3$

N-Methyl-N-(1-propynylthio)-benzenamine (3b); Typical Procedure for N-(1-Alkynylthio)-benzenamines 3a–d, f, h:

To a stirred solution of *N*-methylbenzenamine (**1**, $R^1 = CH_3$, $R^2 = H$; 0.321 g, 3 mmol) in anhydrous tetrahydrofuran (6 ml) under argon at −20 °C is added a 1 molar solution (3.6 ml, 3.6 mmol) of ethylmagnesium bromide in ether. Stirring is continued while the mixture is slowly warmed to 40 °C and then held at this temperature for 30 min (until evolution of ethane is complete). The mixture is then cooled to 0 °C, a solution of 1-propynyl thiocyanate[6] (**2**, $R^3 = CH_3$; 0.231 g, 3 mmol) is added (the mixture turns dark red), and stirring is continued for 2 h at room temperature. Then, saturated sodium chloride solution (20 ml) is added and the mixture is extracted with ether (3 × 20 ml). The organic layer is washed with water (2 × 20 ml) and dried with magnesium sulphate. Removal of the solvent under reduced pressure at room temperature affords product **3b** which was purified by flash chromatography (Kiesel gel Merck 60) using pentane/dichloromethane (95/5) as eluent; yield: 0.249 g (47 %); oil.

N-Ethynylthio-N-methylbenzenamine (3e)[18]:

Commercial potassium fluoride dihydrate (0.283 g, 3 mmol) is added to a stirred solution of *N*-methyl-*N*-(trimethylsilylethynylthio)-benzenamine (**3d**; 0.235 g, 1 mmol) in methanol (10 ml) and stirring

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Table 1. *N*-(1-Alkynylthio)-benzenamines (**3**) prepared

3	Yield[a] [%]	Molecular Formula[b]	M.S. *m/e* (rel. int. %)[c]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]
a	15	C_9H_9NS (163.1)	126 (30); 162 (26); 130 (23); 92 (46); 71 (21); 69 (29); 65 (100); 63 (21)	1.86 (s, 3H); 4.91 (br. s., 1H); 6.70–7.33 (m, 5H)[d]	5.16 (q); 71.41 (s); 99.18 (s); 116.25 (d); 121.32 (d); 129.23 (d); 145.79 (s)[e]
b	47	$C_{10}H_{11}NS$ (177.3)	177 (22); 106 (60); 79 (25); 77 (100); 71 (12); 59 (24); 51 (40)	1.92 (s, 3H); 3.28 (s, 3H); 6.75–7.30 (m, 5H)[d]	5.22 (q); 44.15 (q); 68.29 (s); 102.40 (s); 117.65 (d); 121.07 (d); 128.84 (d); 150.00 (s)[e]
c	51	$C_{16}H_{15}NS$ (253.3)	253 (20); 162 (40); 104 (30); 91 (100); 77 (95); 71 (12); 65 (30); 51 (36)	1.96 (s, 3H); 4.73 (s, 2H); 6.76–7.36 (m, 10H)[d]	5.47 (q); 60.23 (t); 69.00 (s); 101.72 (s); 118.14 (d); 121.17 (d); 127.00 (d); 127.26 (d); 128.14 (d); 128.56 (d); 137.55 (s); 149.30 (s)[e]
d	43	$C_{12}H_{17}NSSi$ (235.35)	235 (25); 115 (20); 106 (100); 105 (36); 79 (35); 77 (36); 75 (24); 73 (85)	0.13 (s, 9H); 3.29 (s, 3H); 6.35–7.40 (m, 5H)[f]	0.10 (q); 43.92 (q); 93.44 (s); 121.40 (d); 128.00 (d); 128.52 (d); 149.5 (s)[g,h]
e	65	C_9H_9NS (163.1)	163 (28); 106 (61); 79 (30); 77 (100)	3.3 (s, 3H); 3.6 (s, 1H); 6.95–7.40 (m, 5H)[f]	44.05 (q); 67.12 (d); 97.41 (s); 121.57 (d); 128.09 (d); 128.60 (d); 149.81 (s)[g]
f	46	$C_{18}H_{21}NSSi$ (311.4)	311 (23); 220 (28); 182 (25); 123 (38); 115 (38); 104 (32); 91 (100); 77 (83); 73 (36)	0.17 (s, 9H); 4.75 (s, 2H); 6.95–7.40 (m, 10H)[f]	0.16 (q); 60.2 (t); 94.38 (s); 118.91 (d); 121.82 (d); 127.19 (d); 127.65 (d); 128.26 (d); 128.65 (d); 137.36 (s); 149.30 (s)[g,h]
g	85	$C_{15}H_{13}NS$ (239.2)	239 (35); 183 (32); 106 (18); 91 (100); 77 (21)	3.63 (s, 1H); 4.76 (s, 2H); 6.95–7.45 (m, 10H)[f]	60.17 (t); 67.32 (d); 98.32 (s); 118.26 (d); 121.18 (d); 127.27 (d); 127.81 (d); 128.30 (d); 128.62 (d); 137.7 (s); 149.6 (s)[g]
h	43	$C_{18}H_{20}ClNSSi$ (345.8)	347 (8); 345 (20); 254 (14); 216 (23); 157 (17); 138 (15); 115 (16); 111 (30); 91 (100); 77 (25); 75 (28); 73 (37)	0.18 (s, 9H); 4.74 (s, 2H); 7.14–7.42 (m, 9H)[f]	3.00 (q); 60.4 (t); 93.76 (s); 120.17 (d); 126.97 (s); 127.36 (d); 127.55 (d); 128.33 (d); 128.56 (d); 136.8 (s); 147.75 (s)[g,h]

[a] Yield after chromatography. All compounds **3** were obtained as undistillable oils.
[b] Satisfactory microanalyses obtained: C ± 0.4, H ± 0.3, N ± 0.3, S ± 0.3.
[c] Recorded on a Nermag R10-10B (direct inlet; E.I. 70 eV).
[d] Recorded on a Varian 90 spectrometer.
[e] Recorded on a Bruker SY 200 spectrometer.
[f] Recorded on a CAMECA 250 spectrometer.
[g] Recorded on a Bruker WH 90 spectrometer.
[h] one C≡ is hidden under the signal of $CDCl_3$.

Table 2. 2-Thioxo-2,3-dihydroindoles (**5**) prepared

5	Yield[a] [%]	Molecular Formula[b] or Lit. Data	M.S. *m/e* (rel. int. %)	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]
b	68	m.p. 45–46°[11,12]	178 (16); 177 (100); 176 (49); 144 (64); 128 (14); 77 (22); 51 (16)	1.55 (d, 3H, J = 7.5 Hz); 3.56 (s, 3H); 3.70 (q, 1H, J = 7.5 Hz); 6.76–7.36 (m, 4H)[d]	18.9 (q); 30.9 (q); 51.9 (d); 108.7 (d); 122.7 (d); 123.4 (d); 127.2 (d); 134.2 (s); 144.3 (s); 205.7 (s)[e]
c	88	$C_{16}H_{15}NS$ (253.3)	253 (66); 220 (55); 162 (26); 144 (19); 128 (36); 91 (100); 77 (43); 65 (65); 51 (38)	1.61 (d, 3H, J = 7.5 Hz); 3.83 (q, 1H, J = 7.5 Hz); 5.38 (s, 2H); 6.45–7.36 (m, 9H)[d]	19.8 (q); 48.1 (t); 52.8 (d); 110.4 (d); 123.6 (d); 124.2 (d); 127.3 (d); 127.8 (d); 128.0 (d); 128.9 (d); 134.9 (s); 135.3 (s); 144.6 (s); 208.1 (s)[f]
e	75	m.p. 109–111°[11]	163 (100); 148 (25); 130 (40); 77 (24)	3.58 (s, 3H); 4.06 (s, 2H); 6.90–7.40 (m, 4H)[g]	31.3 (q); 49.04 (t); 109.36 (d); 112.21 (s); 123.06 (d); 124.06 (d); 127.68 (d); 128.91 (s); 200.3 (s)[e]
g	87	$C_{15}H_{13}NS$ (239.2)	239 (45); 206 (28); 149 (34); 130 (20); 114 (36); 91 (100); 77 (42)	4.10 (s, 2H); 5.33 (s, 2H); 6.48–7.32 (m, 9H)[g]	48.00 (t); 48.29 (t); 110.27 (d); 112.67 (s); 123.73 (d); 123.99 (d); 127.10 (d); 127.55 (d); 128.58 (d); 128.85 (s); 134.41 (s); 201.28 (s)[e]

[a] Yield after chromatography. All compounds **5** were obtained as oils.
[b] Satisfactory microanalyses obtained: C ± 0.4, H ± 0.3, N ± 0.3, S ± 0.3.
[c] Recorded on a Nermag R10-10B (direct inlet; E.I. 70 eV).
[d] Recorded on a Varian 90 spectrometer.
[e] Recorded on a Brucker WH 90 spectrometer.
[f] Recorded on a Bruker SY 200 spectrometer.
[g] Recorded on a CAMECA 250 spectrometer.

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Table 3. 2-Methylthioindoles (**6**) prepared

6	Yield[a] [%]	Molecular Formula[b] or Lit. Data	M.S. *m/e* (rel. int. %)[c]	^{1}H-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS_{int}) δ [ppm]
b	77	oil[11]	192 (11); 191 (88); 177 (12); 176 (100); 144 (14); 143 (12); 132 (16); 117 (12); 115 (13); 77 (14); 51 (11)	2.20 (s, 3H); 2.43 (s, 3H); 3.76 (s, 3H); 6.90–7.48 (m, 4H)[d]	10.1 (q); 20.0 (q); 29.8 (q); 109.1 (d); 116.6 (s); 118.75 (d); 118.8 (d); 122.4 (d); 127.3 (s); 129.0 (s); 137.3 (s)[e]
c	82	$C_{17}H_{17}NS$ (267.3)	267 (34); 91 (100); 77 (28); 65 (30); 51 (21)	2.00 (s, 3H); 2.44 (s, 3H); 5.43 (s, 2H); 6.8–7.6 (m, 9H)[f]	10.2 (q); 20.2 (q); 47.0 (t); 109.9 (d); 117.6 (d); 118.9 (d); 119.1 (d); 122.7 (d); 126.0 (d); 126.8 (d); 127.6 (s); 128.4 (d); 129.17 (s); 137.0 (s); 138.3 (s)[e]
e	80	oil[11]	177 (100); 162 (90); 128 (28); 118 (36); 89 (26); 77 (34); 63 (25)	2.42 (s, 3H); 3.76 (s, 3H); 6.58 (s, 1H); 7.10–7.60 (m, 4H)[d]	
g	83	$C_{16}H_{15}NS$ (253.1)	253 (25); 118 (12); 91 (100); 65 (20)	2.32 (s, 3H); 5.46 (s, 2H); 6.68 (s, 1H); 7.0–7.64 (m, 9H)[d]	

[a] Yield after chromatography.
[b] Satisfactory microanalyses obtained: C ± 0.4, H ± 0.3, N ± 0.3, S ± 0.3.
[c] Recorded on a Nermag R10-10B (direct inlet; E.I. 70 eV.).
[d] Recorded on a CAMECA 250 spectrometer.
[e] Recorded on a Bruker WH-90 spectrometer.
[f] Recorded on a Varian 90 spectrometer.

is continued for 30 min at room temperature. A large part of the solvent is removed under reduced pressure; water (20 ml) is added and the mixture is extracted with dichloromethane (3 × 15 ml). The organic layer is washed with water (2 × 15 ml) and dried with magnesium sulphate. Removal of the solvent under reduced pressure at room temperature affords product **3e** which is purified by flash chromatography (Kieselgel Merck 60) using pentane/dichloromethane (90/10) as eluent; yield: 0.106 g (65%); oil.

N-Benzyl-N-ethynylthiobenzenamine (**3g**) is obtained from the silyl derivative **3f** in an analogous manner.

2-Thioxo-2,3-dihydroindoles (5b, c, e, g); General Procedure:
A solution of the *N*-(1-alkynylthio)-benzenamine **3** (1 mmol) in anhydrous benzene (10 ml) under argon is heated under reflux for 3 h (**3b, c**) or 90 min (**3e, g**). The solvent is then removed and the residual oil purified by flash chromatography (Kiesel gel Merck 60) using pentane/dichloromethane 60/40 as eluent.

1,3-Dimethyl-2-methylthioindole (6b); Typical Procedure for 2-Methylthioindoles 6b, c, e, g:
To a stirred solution of 1,3-dimethyl-2-thioxo-2,3-dihydroindole (**5b**; 0.177 g, 1 mmol) in dry acetone (10 ml) are added potassium carbonate (0.140 g; 1 mmol) and iodomethane (0.570 g, 4 mmol). After stirring for 15 h at room temperature, the mixture is filtered. Removal of solvent from the filtrate yields the crude product **6b** which is purified by flash chromatography (Kiesel gel Merck 60) using pentane/dichloromethane (80/20) as eluent; yield: 0.147 g (77%); oil.

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